THE THERMAL CONDUCTIVITY OF PURE WATER AND STANDARD SEA WATER AS A FUNCTION OF PRESSURE AND TEMPERATURE. PART II. PURE WATER

V. John Castelli, et al

Naval Ship Research and Development Center
Annapolis, Maryland

October 1972
Best Available Copy
The Thermal Conductivity of Pure Water and Standard Sea Water as a Function of Pressure and Temperature
Part II - Pure Water

by

V. John Castelli and E. M. Stanley

Approved for public release; distribution unlimited.

October 1972

Report 3566-II
The Naval Ship Research and Development Center is a U.S. Navy center for laboratory effort directed at achieving improved sea and air vehicles. It was formed in March 1967 by merging the David Taylor Model Basin at Carderock, Maryland with the Marine Engineering Laboratory at Annapolis, Maryland.

Naval Ship Research and Development Center
Bethesda, Md. 20034

MAJOR NSRDC ORGANIZATIONAL COMPONENTS

NSRDC
COMMANDER 00
TECHNICAL DIRECTOR 01

OFFICER-IN-CHARGE
CARDEROCK 05

OFFICER-IN-CHARGE
ANNAPOLIS 04

SYSTEMS
DEVELOPMENT
DEPARTMENT 11

SHIP PERFORMANCE
DEPARTMENT 15

AVIATION AND
SURFACE EFFECTS
DEPARTMENT 16

STRUCTURES
DEPARTMENT 17

COMPUTATION
AND MATHEMATICS
DEPARTMENT 18

SHIP ACOUSTICS
DEPARTMENT 19

PROPULSION AND
AUXILIARY SYSTEMS
DEPARTMENT 27

MATERIALS
DEPARTMENT 26

CENTRAL
INSTRUMENTATION
DEPARTMENT 29
The Thermal Conductivity of Pure Water and Standard Sea Water as a Function of Pressure and Temperature

II - Pure Water

V. J. Castelli and E. M. Stanley

October 1972

Task Area SF52-552-101

Task 12874

Work Unit 1-2853-101

Approved for public release; distribution unlimited.

Results of the experimental observations of the thermal conductivity of pure water for the pressure range of atmospheric to 1400 bars and temperature from 0°-30° C are presented. Data were obtained with a concentric cylinder apparatus and have an estimated accuracy of about 1%. These data are compared with those previously reported in the literature. Historical relationships proposed to describe the behavior of the thermal conductivity are investigated, and their inadequacy noted.

(Authors)
<table>
<thead>
<tr>
<th>KEY WORDS</th>
<th>LINK A</th>
<th></th>
<th>LINK B</th>
<th></th>
<th>LINK C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ROLE</td>
<td>WT</td>
<td>ROLE</td>
<td>WT</td>
<td>ROLE</td>
<td>WT</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td>Thermal conductivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td></td>
<td></td>
<td>Temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apparatus</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ABSTRACT

Results of the experimental observations of the thermal conductivity of pure water for the pressure range of atmospheric to 1400 bars and temperatures from 0°-30° C are presented. Data were obtained with a concentric cylinder apparatus and have an estimated accuracy of about 1%. These data are compared with those previously reported in the literature. Historical relationships proposed to describe the behavior of the thermal conductivity are investigated, and their inadequacy noted.
ADMINISTRATIVE INFORMATION

This report is part of Task Area SF52-552-101, Task 12874, Work Unit 1-2853-101, as described in the 1 July 1972 Program Summary.

The mention of proprietary products or devices by name in no way implies that they are endorsed by the U. S. Navy to the exclusion of other similar products or devices, nor may such mention be made in commercial advertising.
TABLE OF CONTENTS

ABSTRACT iii
ADMINISTRATIVE INFORMATION iv
INTRODUCTION 1
EXPERIMENTAL INVESTIGATION 1
PRECISION, ACCURACY, AND ERROR ANALYSIS 1
RESULTS 3
DISCUSSION 4
THEORETICAL RELATIONSHIPS 5
CONCLUSIONS 7
TECHNICAL REFERENCES 8
LIST OF FIGURES

Figure 1 - Graph; Experimental Data for the Thermal Conductivity of Pure Water as a Function of Pressure for Various Temperatures
Figure 2 - Graph; Thermal Conductivity of Pure Water as Determined by Equation of Least Squares for Experimental Data
Figure 3 - Graph; Comparison of Powell's Proposed Values for Thermal Conductivity of Pure Water at Atmospheric Pressure with Results of these Experiments
Figure 4 - Graph; Historical Determination of the Effect of Pressure on the Thermal Conductivity of Pure Water for a Temperature of 30° C
Figure 5 - Graph; Historical Determination of the Effect of Pressure on the Thermal Conductivity of Pure Water for a Temperature of 0° C

INITIAL DISTRIBUTION
INTRODUCTION

A continuing part of the oceanographic research at this laboratory is the determination of the physical and chemical properties of sea water and water at pressure. Projects previously completed have included viscosity and refractive index measurements at pressure. Most recently, measurements of the thermal conductivity of sea water and pure water have been completed in the temperature range of $0^\circ-30^\circ$ C* and the pressure range of 0-1400 bars. This report is the second part of a series and describes the results of the experimental measurements of the thermal conductivity of pure water.

EXPERIMENTAL INVESTIGATION

Determinations of the thermal conductivity of pure water were conducted for temperatures of $+1.83^\circ$, $1.86^\circ$, $10.32^\circ$, $11.68^\circ$, $20.28^\circ$, $21.76^\circ$, $30.28^\circ$, and $31.70^\circ$ C, and nominal pressures of 10, 25, 200, 400, 600, 800, 1000, 1200, and 1400 bars.

The cleaning, filling, and experimental setup and procedures for the use of the special high-pressure vessel have been previously described. The water used for these measurements was freshly distilled and deionized, with a specific conductance of 0.47 micromhos/cm. The purity of the water was not judged to be extremely critical on the basis of Riedel's findings which showed minimal effects for salt in aqueous solution.

PRECISION, ACCURACY, AND ERROR ANALYSIS

Two distinct series of measurements were conducted by utilizing different thermocouple junctions. Each series consisted of at least three determinations of each data point and many determinations of selected "reference" data points, primarily at 10 and 25 bars pressure. In almost all cases, the data resulting from any particular series agrees to within 0.2% of the mean value. This small variation was traced to the procedure used to measure the temperature differential. The setup required solder joints to mate the thermocouple leads to the high-pressure electrical feedthroughs. These joints required unsoldering and resoldering during each assembly of the apparatus. This was observed to cause a variation in the thermocouple electromotive force (EMF) of 0.5 uv, which is $\pm 0.2\%$ of the approximately 130-150 uv generated by the temperature gradient. The accuracy of thermocouple differential temperature measurement can only be estimated and is thought to be $\pm 0.5\%$, based upon comparison of the results.

*Abbreviations used in this text are from the GPO Style Manual, 1967, unless otherwise noted.

1 Superscripts refer to similarly numbered entries in the Technical References at the end of the text.
obtained with both sets of thermocouples. This estimate is believed to be conservative because of the short temperature differential (<1.0° C) and because the increase of the EMF/degree is not rapid. The EMF values used to calibrate the thermocouples and generate the least squares 10th degree interpolation polynomial were obtained from the National Bureau of Standards. These values will be incorporated into a new circular, as yet unpublished, which supercedes NBS circular 561.

The temperature bath around the pressure vessel was controlled to ±0.01° C and measured with a quartz crystal thermometer with an absolute accuracy (after ice point calibration) of ±0.05° C. An error of ±0.05° C in this measurement results in an inaccuracy of ±0.02% in K, the thermal conductivity constant.

The pressure was measured with Heise pressure gages that were calibrated to ±0.1%. A variation of ±0.1% would result in an error in K of ±0.06%.

The power measurement consisted of independent determinations of both voltage and current. The minimum accuracy of the voltage measurement is ±0.06%, while that for current is ±0.12%.

The measurements used to deduce the cell constant contribute an error of ±0.18% based upon a maximum measurement error of ±7 parts in 100,000.

Finally, heat-loss errors which were kept to a minimum through design are estimated to result in an error of ±0.1%.

The total error for which corrections cannot be applied is therefore calculated to be ±1.04%, or between 5.5 x 10⁻⁵ and 6.5 x 10⁻⁵ watts/cm-degree, depending upon the value of K.

The single error for which correction of experimental results is possible is concerned with the placement of the thermocouple probes. Through design limitations, thermocouples could not be placed directly at the surface of the liquid. This finite distance contributed errors of from 1.35% to 1.60%, depending upon the value of K which changed in relation to temperature and pressure of the fluid. In all calculations, the thermal conductivity of silver, Kₙ, was taken as a constant with respect to pressure and temperature at 4.209 watts/cm-degree; d₁, the average distance between the three inner probes and the inner surface of the liquid, equal to 0.210 cm (0.083 inch); and d₂, the average distance between the outer probes and the outer surface of the liquid, equal to 0.292 cm (0.115 inch). The actual calculation of K for the liquid was accomplished using the formula:

\[ 2πL \Delta T = V I \left[ \frac{\ln \frac{r_o}{r_0 - d_1}}{K_s} + \frac{\ln \frac{r}{r_0}}{K} + \frac{\ln \frac{r}{r + d_2}}{K_s} \right], \quad (1) \]
where

\[ L = \text{length of thermally conductive fluid path} \]
\[ \Delta T = \text{total temperature drop observed experimentally} \]
\[ V = \text{voltage drop across the heater} \]
\[ I = \text{current through the heater} \]
\[ r_o = \text{internal radius of fluid annulus} \]
\[ r = \text{external radius of fluid annulus} \]
\[ K = \text{thermal conductivity of fluid} \]
\[ K_s = \text{thermal conductivity of silver} \]
\[ d_1 = \text{distance from inner thermocouples to inner surface of fluid} \]
\[ d_2 = \text{distance from outer thermocouples to outer surface of fluid} \]

RESULTS

The corrected experimental results of the measurements are listed in table 1 and shown graphically in figure 1.

| TABLE 1 |
|---|---|---|---|---|---|---|---|---|---|
| THERMAL CONDUCTIVITY \((10^{-5} \text{ WATTS/CN-DEGRE})\) FOR TEMPERATURES OF \(1.83^\circ\text{C}-31.70^\circ\text{C}\) AND PressURES TO 1400 BARS AS MEASURED BY IRON- AND CHROMEL-CONSTANTAN THERMOCOUPLES |
| Cage Pressure Bars | \(1^{(1)}\) | \(1^{(2)}\) |
|---|---|---|---|---|---|---|---|---|
| Temperature, \(^\circ\text{C}\) | 1.83 | 10.32 | 20.28 | 30.26 | 40.66 | 51.66 | 61.76 | 71.70 |
| 10 | 563.0 | 580.5 | 597.0 | 611.3 | - | - | - | - |
| 25 | - | - | - | - | 560.0 | 581.0 | 596.5 | 611.0 |
| 200 | 572.0 | 588.0 | 605.0 | 616.0 | 568.0 | 569.5 | 604.0 | 619.0 |
| 400 | 589.5 | 597.5 | 613.5 | 627.5 | 577.5 | 598.5 | 611.5 | 627.0 |
| 600 | 589.0 | 606.0 | 622.0 | 635.0 | 585.5 | 607.0 | 621.0 | 635.5 |
| 800 | 597.0 | 614.0 | 630.5 | 643.5 | 594.5 | 615.5 | 628.5 | 643.5 |
| 1000 | 604.0 | 623.5 | 638.0 | 653.0 | 604.0 | 622.0 | 639.0 | 652.0 |
| 1200 | 612.0 | 630.0 | 647.0 | 659.5 | 613.0 | 632.0 | 648.5 | 660.5 |
| 1400 | (3) | 639.5 | 654.5 | 668.5 | (3) | 642.0 | 655.5 | 669.0 |

1. Measured by Iron - Constantan thermocouple junctions.
2. Measured by Chromel - Constantan thermocouple junctions.
3. Leaking seals - no reading taken.
The data can be represented as a function of temperature and pressure by the equation:

\[ K = 5.5780 \times 10^{-3} + 4.249 \times 10^{-7}P + 2.223 \times 10^{-5}T - 1.797 \times 10^{-7}T^2, \tag{2} \]

where \( K \) is given in watts/cm-degree, \( P \) is the pressure in bars, and \( T \) is the temperature in °C. The values generated by this equation are given in table 2 and shown graphically in figure 2. These have a standard error of ±1.5 \( \times 10^{-5} \) watts/cm-degree, or ±0.25% from the experimental data.

<table>
<thead>
<tr>
<th>Gage Pressure</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>bars</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>557.5</td>
</tr>
<tr>
<td>200</td>
<td>565.0</td>
</tr>
<tr>
<td>400</td>
<td>574.5</td>
</tr>
<tr>
<td>600</td>
<td>583.0</td>
</tr>
<tr>
<td>800</td>
<td>591.5</td>
</tr>
<tr>
<td>1000</td>
<td>600.0</td>
</tr>
<tr>
<td>1200</td>
<td>608.5</td>
</tr>
<tr>
<td>1400</td>
<td>617.0</td>
</tr>
</tbody>
</table>

**DISCUSSION**

Direct comparison of the data in table 2 with that reported in the literature is only partly possible because most data for high pressure covers higher temperature ranges, and that for lower temperatures is restricted to low pressures.

Powell's review and analysis of all the atmospheric pressure determinations has resulted in a set of "most probable" values for water. These data are shown in figure 3 in comparison to our atmospheric values, as determined from equation (1). It can be seen that our results are systematically about 0.5%-1% lower than those "most probable" values cited by Powell. While the origin of this discrepancy is unknown, no special effort was made to resolve this difference since we are primarily concerned with the effect of pressure on the thermal conductivity.
Previous determinations of the thermal conductivity of water at high pressure have been conducted by Bridgeman, Lawson, et al., and Timrot and Vargaftik; however, the overlap with our data is sparse. Figure 4 shows the data of Bridgeman (corrected in accordance with the recommendations of Riedel), Lawson, et al., and our results for a temperature of 300°C. All results agree closely with slopes of 3.7 x 10^-7, 3.9 x 10^-7, and 4.2 x 10^-7 watts/cm-degree-bar, respectively. In addition, our absolute results are in excellent agreement (±0.5%) with those given by Lawson.

The data obtained by Timrot and Vargaftik for 0°C for pressures to 400 atmospheres appear in figure 5, along with ours for the same temperature. Both sets of results agree within 1% of each absolutely, with slopes of 4.1 x 10^-7 and 4.2 x 10^-7 watts/cm-degree-bar, respectively.

THEORETICAL RELATIONSHIPS

Relationships between thermal conductivity and other physically measurable quantities have been advanced on the basis of both empirical and theoretical groundwork.

One of the earliest relationships known was that proposed by Weber. He introduced an empirical formula which was later theoretically deduced by Predvoditelev, and relates density (ρ), specific heat at constant pressure (C_p), and molecular weight (m), and the thermal conductivity (K), to a constant (A). The formula is:

$$ K = A \left( \frac{m}{C_p \rho} \right)^{1/3} $$  \hspace{1cm} (3)

The value of this constant as computed from our conductivity data, and values of C_p and ρ as taken from the literature, can be seen in table 3 for pressures up to 1000 bars. It is evident that this equation is not valid for the pure water system.

Another relationship is that given by Bridgeman, relating the thermal conductivity (K), to the density (ρ), the absolute weight of a molecule (m), the velocity of sound in the medium (v), and the Boltzmann gas constant (k), by

$$ K = 2kv \left( \frac{\rho}{m} \right)^{2/3} $$  \hspace{1cm} (4)
TABLE 3
VALUES OF THE CONSTANT A AS DETERMINED FROM WEBER'S FORMULA

<table>
<thead>
<tr>
<th>Gage Pressure bars</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>346.6</td>
</tr>
<tr>
<td>200</td>
<td>355.0</td>
</tr>
<tr>
<td>400</td>
<td>362.7</td>
</tr>
<tr>
<td>600</td>
<td>369.9</td>
</tr>
<tr>
<td>800</td>
<td>376.5</td>
</tr>
<tr>
<td>1000</td>
<td>382.7</td>
</tr>
</tbody>
</table>

However, this relationship yields values of K only about two thirds of the experimental values for thermal conductivity. Bridgeman's value of $2.02 \times 10^{-16}$ ergs/degree for the Boltzmann gas constant, $k$, is in error by almost 50% and accounts for the rather close agreement between his calculated and experimental values. This equation, when quoted by El'Darov,10 is given in the slightly different form of

$$K = 3kv \left(\frac{\rho}{m}\right)^{2/3}.$$  (5)

Because of the discrepancy between equations (4) and (5) concerning the value of the constant, we decided to evaluate its magnitude according to our values for the thermal conductivity, such that

$$\frac{K}{kv} \left(\frac{m}{\rho}\right)^{2/3} = B.$$  (6)

Values for B are tabulated at pressures to 1000 bars, the limit of other available data, in table 4. It is obvious from this table that B is constant neither with respect to temperature, nor pressure.

An equation given by Vargaftik11 expresses the temperature dependence of thermal conductivity of liquids as

$$K = C_p^{4/3},$$  (7)
where \( K \) and \( p \) have their usual meanings, and \( C \) is a constant dependent upon pressure. Table 5 gives values of \( C \) based upon our experiments. It is again quite evident that this equation is not valid for the pure water system.

**TABLE 4**
VALUES FOR THE CONSTANT \( B \) FROM EQUATION (6)

<table>
<thead>
<tr>
<th>Gage Pressure bars</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>2.774</td>
</tr>
<tr>
<td>200</td>
<td>2.736</td>
</tr>
<tr>
<td>400</td>
<td>2.696</td>
</tr>
<tr>
<td>600</td>
<td>2.655</td>
</tr>
<tr>
<td>800</td>
<td>2.615</td>
</tr>
<tr>
<td>1000</td>
<td>2.577</td>
</tr>
</tbody>
</table>

**TABLE 5**
VALUES FOR THE CONSTANT \( C \) IN EQUATION (7)

<table>
<thead>
<tr>
<th>Gage Pressure bars</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>179.3</td>
</tr>
<tr>
<td>200</td>
<td>179.0</td>
</tr>
<tr>
<td>400</td>
<td>178.6</td>
</tr>
<tr>
<td>600</td>
<td>178.1</td>
</tr>
<tr>
<td>800</td>
<td>177.5</td>
</tr>
<tr>
<td>1000</td>
<td>176.8</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

- The reported thermal conductivity of pure water is in excellent agreement with historical data thus giving credence to the design and techniques used.
Thermal conductivity of pure water is a direct linear function of pressure throughout the pressure and temperature range investigated.

Previously proposed equations relating thermal conductivity to other measurable bulk properties have failed to accurately describe the pure water system.

TECHNICAL REFERENCES

11 - Vargaftik, N. B., Thesis, BNIN, USSR Academy of Sciences (1951)
Figure 1
Experimental Data for the Thermal Conductivity of Pure Water as a Function of Pressure for Various Temperatures

○ RESULTS OBTAINED WITH IRON-CONSTANTAN THERMOCOUPLES
◆ RESULTS OBTAINED WITH CHROMEL-CONSTANTAN THERMOCOUPLES
Figure 2
Thermal Conductivity of Pure Water as Determined by Equation of Least Squares for Experimental Data
Figure 3
Comparison of Powell's Proposed Values for Thermal Conductivity of Pure Water at Atmospheric Pressure with Results of These Experiments.
**Figure 4**
Historical Determination of the Effect of Pressure on the Thermal Conductivity of Pure Water for a Temperature of 30° C

**Figure 5**
Historical Determination of the Effect of Pressure on the Thermal Conductivity of Pure Water for a Temperature of 0° C